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(54) Ethylenic monomer polymerization process

(57) In the bulk or suspension polymerization of vinyl monomers, particularly vinyl chloride, t-amyl peroxypivalate is employed as the initiator.

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SPECIFICATION

Ethylenic monomer polymerization process

This invention relates to a process for the polymerization of various ethylenically unsaturated monomers, particularly vinyl chloride, in bulk or suspension systems, using a t-amyl peroxypivalate as the initiator.

The suspension polymerization of vinyl chloride is generally carried out at temperatures below 70°C using organic soluble initiators. Although lauroyl peroxide was earlier the most widely used catalyst, in recent years other low temperature catalysts including azobisisobutyrontrile, diisopropyl peroxydicarbonate, t-butyl peroxypivalate and mixtures thereof have come into common usage.

The choice of initiator requires consideration of the nature of the catalyst and its influence on the polymerization process and the properties of the poly(vinyl chloride) produced thereby.

The polymerization of vinyl chloride is characterized by a short induction period, followed by a gradually increasing rate of polymerization. During the earlier stages of the polymerization, the reaction rate is lower than the maximum so that the capacity of the reactor is not fully utilized. A suitable initiator must reduce the induction period and, due to a more constant rate of polymerization, increase reactor productivity. Further, a suitable initiator will be one which can generally be used at relatively low levels which will give a low order of chain branching during polymerization.

Although certain peroxyesters such as diisopropyl peroxydicarbonate are known for and offer advantages in vinyl chloride polymerization, their disadvantages include a long induction period, a non-uniform polymerization rate, the necessity for low temperature shipping and storage and decreased efficiency at elevated temperatures. The development of an initiator which offers the noted advantages without the accompanying disadvantages is a matter of ongoing concern in the vinyl chloride polymerization field.

Summary of the Invention

An object of the present invention is to provide a process for the polymerization of ethylenically unsaturated monomers, particularly vinyl chloride, in the presence of a peroxygen compound which is not subject to the known disadvantages of conventional peroxide initiators at temperatures at which the peroxide is stable and readily handled. Another object of the present invention is to provide a process for the bulk or suspension polymerization of vinyl chloride at temperatures below 70°C using a suitable peroxygen compound as the initiator.

It has now been found that this improvement in unsaturated monomer, particularly vinyl chloride, polymerization can be achieved by utilizing as the initiator t-amyl peroxypivalate.

Detailed Description of the Invention

According to the present invention, the polymerization of ethylenically unsaturated monomers, particularly vinyl chloride, is carried out in bulk or suspension, under the conditions applicable thereto and well known to those skilled in the art, using a catalyst system comprising t-amyl peroxypivalate as the initiator. While the use of t-amyl peroxypivalate alone as the initiator has been found to give eminently satisfactory results, it can be used in conjunction with other known initiators or modifiers where desired.

It has been found that the use of t-amyl peroxypivalate provides equally satisfactory results in either bulk or suspension polymerizations of ethylenically unsaturated monomers.

In general, t-amyl peroxypivalate will generally be employed at a concentration of from about 0.01 to about 5.0% by weight of the vinyl monomer, with a range of from about 0.05 to about 1.0% by weight as the preferred concentration.

The procedures normally used in the bulk and suspension polymerization of vinyl chloride are applicable to the process of the present invention. Typical procedures are described in Encyclopedia of Polymer Science and Technology, *14*, 339—343 (1971), the disclosure of which is incorporated herein by reference.

The polymerization may be conducted at or above atmospheric pressure. In the usual procedure, the reactor is charged at atmospheric pressure and the pressure rises when the contents of the reactor are brought to reaction temperature. The pressure may increase further due to the reaction exotherm and then remain constant until the conversion reaches about 70%, after which it decreases rapidly as the reaction continues.

The polymerization temperature may range from —50° to +70°C for bulk polymerization, although temperatures of 40° to 60°C are preferred. Suspension polymerization may be carried out at temperatures of +5° to +70°C, although preferred temperatures are in the 20—60°C range.

The concentrations of monomer and water, e.g. about 2/1 weight ratio, and the types and concentrations of suspending agents are those normally used in suspension polymerization and are well known to those skilled in the art. Typical suspending agents include poly(vinyl alcohol), partially saponified poly(vinyl acetate), gelatin, methylcellulose, vinyl acetate-maleic anhydride copolymer and the like. Various emulsifiers such as sulfonated oils and ethylene oxide condensation products may be added to control surface tension and particle shape. Buffers may be used where necessary, e.g. when gelatin is used as suspending agent. Chain transfer agents such as chlorinated hydrocarbons and isobutylene may be used in the preparation of low molecular weight polymer.

Although the peroxygen initiator of the present invention is particularly useful in the bulk and

suspension polymerization of vinyl chloride, it can also be used in the copolymerization of vinyl chloride with vinylidene chloride, vinyl acetate and other monomers which undergo copolymerization with vinyl chloride.

The homopolymerization and copolymerization of other ethylenically unsaturated monomers may be carried out with the peroxygen initiator of the present invention. Representative monomers include ethylene, vinylidene chloride, styrene, vinyl-toluene, α-methylstyrene, p-chlorostyrene, p-chloromethylstyrene, butadiene, isoprene, piperylene, chloroprene, vinyl acetate, vinyl propionate, vinyl benzoate, acrylic and methacrylic esters including methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, lauryl methacrylate, octadecyl methacrylate, acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, maleic anhydride and the like. Such ethylenically unsaturated monomers are well known to those skilled in the art and undergo homopolymerization and copolymerization in the presence of the peroxygen initiator of the present invention.

The following example is an illustrative embodiment of the practice of the present invention and is not to be construed as a limitation on the invention or the claims. Numerous modifications will be obvious to those skilled in the art.

EXAMPLE 1

A 2 liter stainless steel autoclave, equipped with agitation means and temperature control, is charged with the following suspension recipe:

630 g deionized water

30 ml of 1% aqueous solution of Methocel F-50

30 ml of 1% aqueous solution of Tween 60

30 ml of 1% aqueous solution of Span 60.

Tween 60 is polyoxyethylene sorbitan monostearate (Atlas Chemical Industries Inc.), Span 60 is sorbitan monostearate (Atlas Chemical Industries Inc.) and Methocel F-50 is methylcellulose having a viscosity of 50 cps at 20°C as a 2% aqueous solution (Dow Chemical Co.). Nitrogen was bubbled through the aqueous solution for 15 minutes.

0.3 g of t-amyl peroxypivalate is then charged to the reactor following which 300 g of distilled liquefied vinyl chloride is pressurized into the reactor. The contents of the reactor were maintained at 50°C with agitation for a period of 9 hours. The resulting polymer product is collected at a yield of 88%.

CLAIMS

1. A process for the preparation of polymers and copolymers of ethylenically unsaturated monomers, which comprises polymerizing at least one such monomer, in bulk or suspension, in the presence of a catalyst system containing as initiator t-amyl peroxypivalate.

2. A process according to claim 1 wherein said monomer is vinyl chloride.

3. A process according to claim 1 or 2 wherein the polymerization is carried out at a temperature of from −50° to +70°C.

4. A process according to claim 3 wherein said polymerization temperature is between 20° and 60°C.

5. A process according to any one of claims 1 to 4 wherein t-amyl peroxypivalate is present at a concentration of from 0.01 to 5.0% by weight of the polymer.

6. A process according to claim 5 wherein t-amyl peroxypivalate is present at a concentration of from 0.05 to 1.0% by weight of the polymer.

7. A process according to claim 1 substantially as described with reference to the Example.

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